Transfer and degradation of polyacrylamide based flocculants in hydrosystems: a review

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Abstract

The aim of this review was to summarize information and scientific data from the literature dedicated to the fate of PAM-based flocculants in hydrosystems. Flocculants, usually composed of polyacrylamides (PAMs), are widely used in several industrial fields, particularly in minerals extraction, to enhance solid/liquid separation in water containing suspended matter. These polymers can contain residual monomer of acrylamide (AMD) which is known to be a toxic compound. This review focuses on the mechanisms of transfer and degradation, which can affect both PAM and residual AMD, with a special attention given to the potential release of AMD during PAM degradation. Due to PAM ability to adsorb onto mineral particles, its transport in surface water, groundwater and soils is rather limited and restricted to specific conditions. PAM can be also subject of biodegradation, photodegradation and mechanical degradation but most of the studies report slow degradation rates without AMD release. In the contrary, the adsorption of acrylamide onto particles is very low, which could favor its transfer in surface waters and ground water. However AMD transfer is likely to be limited by quick microbial degradation.

Key words: flocculation, polyacrylamide, acrylamide, environmental hazards, transfer, adsorption, photodegradation, biodegradation, amidase

1. Introduction

Flocculants are widely used in several industrial fields (mineral extraction, chemical industry, food processing industry, treatment of drinking water, etc.) to enhance solid/liquid separation in water containing suspended matter (Heath *et al.*, 2006, Harford *et al.*, 2011). In most cases, flocculants are polymers composed of polyacrylamide (PAM) (Taylor *et al.*, 2002). PAM is a polymer with high molecular weight, synthetized from acrylamide (AMD) and acrylic acid/acrylate (AA) (Scott *et al.*, 1996; Caulfield *et al.*, 2002). The use of flocculants enables to increase the recycling rate of process water and to decrease sludge volumes and thus the surface of settling ponds. Those ponds are open systems with possible exchanges into the near aquatic environment (water percolation towards soils and aquifers, water seepages in natural streams or rivers…), which can lead to the dissemination of flocculants into surface and groundwaters (de Rosemond & Liber, 2004; Liber *et al.*, 2005). The question of flocculants safety is now arising as a new key-environmental issue. The potential environmental hazard does not concern the polyacrylamide itself, which is generally considered as not toxic (Andersen, 2005), but the products of PAM degradation and the residual acrylamide contained in the flocculants due to incomplete polymerization process (Labahn *et al.*, 2010; Young *et al.*, 2007; Caulfield *et al.*, 2002). AMD is reported to be a neurotoxin to humans (McCollister *et al.*, 1964). AMD is also classified as a carcinogenic (level 2), mutagenic (level 2) and reprotoxic (level 3) compound (World Health Organization 1985; Molak, 1991). This review focuses on the fate of PAM-based flocculants in hydrosystems, with a major emphasis on the mechanisms of transfer and degradation which can affect both PAM and associated AMD. The section dedicated to transfer phenomenon will especially examine transport and reactivity with solid matrices. In the section devoted to degradation, abiotic and biotic factors will be discussed with a specific emphasis on potential hazardous AMD release during PAM degradation.

2. Polyacrylamide and acrylamide in flocculation processes and potential environmental hazards

The word polyacrylamide and the acronym “PAM” (for polyacrylamide) refer to a group of water soluble molecules formed by polymerization of acrylamide monomers. PAMs have been used for decades in a variety of industries and have proven particularly effective in facilitating the solid-liquid separation for waste and drinking water treatment as well as for the clarification of various types of

effluents. High molecular weight PAMs (10^6 to 10^7 $g.mol^{-1}$) work as flocculants by causing suspended particles to bind together to form larger aggregates which can settle out quickly from solution leaving a clear supernatant (Heath *et al.*, 2006). By increasing solid-liquid separation, PAMs improve water clarification processes and water quality prior to discharge, re-use or disposal. In France, for instance, the consumption of PAM-based flocculants is about 15 kt per year. In particular, the aggregate production uses about 900 t/y of PAM-based flocculants (i.e. 6% of the total consumption) as clarification aid (UNPG 2013).

High molecular weight PAMs can be modified to develop non-ionic, anionic, or cationic properties for specific uses (Scott *et al.*, 1996). However for environmental applications which are described in this article, anionic PAMs are preferred because of their extremely low aquatic toxicity compared to cationic forms (Hamilton *et al.*, 1994; de Rosemond & Liber, 2004; Liber *et al.*, 2005). Common anionic PAMs are usually produced by copolymerization of acrylamide and acrylic acid or one of its salts (see Fig.1). Their molecular weights vary between 3.10^6 and 2.10^7 Da. The most polyvalent anionic PAM contains around 30% of acrylate (in mol).

Anionic PAMs used in flocculation applications are water-soluble and have little if any cross-linking. The molecules, when dissolved in water, are nominally linear, although they may be coiled or curled to varying degree due to either substitution along the chain or as a result of electrolytes in the solvating water (Sokja *et al*. 2007).

PAMs can be manufactured to have different molecular weights and charge densities by varying the reaction parameters and/or the relative quantities of reagents used. The charge density of PAM is often expressed as percent anionic, referring to the percentage of its monomers that contain a charged functional group. The variations can result in significant differences in the extent to which PAM will bind to different types of particles, and thus influence the flocculation efficiency. Even among products that contain anionic PAM as their active ingredient, performance can vary substantially if the PAM charge densities or molecular weights are different.

One of the primary areas of concern associated with the use of PAMs is the presence of residual monomer of AMD in the polymer product, due to incomplete polymerization process. AMD is solid at room temperature, highly soluble in water, has a low potential to partition to organic matter, and has a low volatilization potential in water. Acrylamide, often referred by the acronym AMD, is considered to be a likely human carcinogen and neurotoxin (EPA US 2010). All PAMs contain some level of residual

AMD. However, the amount of residual AMD can vary substantially depending on what measures were taken during the manufacturing process to maximize the extent of polymerization. Within the EU, all PAMs are required to contain less than 0.1% (w/w) of residual AMD (European Parliament 1999) unless they are classified and labeled as a Category 2 carcinogen (European Parliament 2006). More stringent thresholds are also set depending on additional regulations covering specific uses like, for example, when PAM-based flocculants are used for the treatment of drinking water (no more than 0.05% of residual AMD). Most of the commercial PAMs products complied with this requirement, even when they are not marketed for drinking water treatment. Knowledge about the fate of PAM and associated residual AMD in hydrosystems (transfer, reactivity…) is limited or non-existent in the field of the use of PAM as a flocculating agent for the treatment of waters. This monomer is water soluble and unlikely to adsorb to organic and inorganic soil components, potential for leaching and groundwater contamination are often considered as the major environmental risk associated with the use of PAMs as flocculants. Several publications have discussed the aquatic toxicity of anionic PAM in the framework of the struggle against agricultural soil erosion where PAMs are used for soil stabilization (Barvenik 1994; Seybold 1994; Entry *et al*. 2002; Sojka *et al*. 2000, 2007). These articles have disregarded its toxicity potential, based largely on theoretical grounds such as the expectation that toxicity would be mitigated by the complexation with dissolved organic matter (Goodrich *et al*. 1991), because any PAM leaving the field would be rapidly adsorbed to soils (Lentz *et al*. 2002), and also because the size of the molecule would prevent passage across biological membranes (Stephens 1991). Few authors have also studied the fate of associated residual AMD when PAMs are used for soil stabilization and demonstrated that in this context AMD undergoes a quick degradation, which prevents its dispersion in the environment (Labahn *et al.*, 2010; Arrowood, 2008, Shanker *et al.*, 1998; Lande *et al.*, 1979). Even if these studies are an important source of information, their results and conclusions cannot be transposed directly to the field of PAM-based flocculants because the phenomenon that can affect the fate of PAM and associated AMD are slightly different and because PAMs used for both applications have different properties (molecular weight and charge densities). It must also be noted that in the field of flocculation, the main vector of dispersion of PAM and AMD in the environment is water, whether surface or groundwater. In the following parts of this article, the mechanisms of PAM and AMD transfer and degradation will be thoroughly reviewed and their potential impacts on the fate of PAM-based flocculants in hydrosystems will be assessed.

3. Transfer of PAM –based flocculants in hydrosystems

3.1. Sorption mechanisms

A variety of PAM and AMD molecular and environmental properties interact to affect their transfer in hydrosystems. These interactions can be significant given the range of PAM use in the environment and the number of environmental and application factors that can vary. Studies related to the environmental fate of PAM have been conducted in the framework of several uses of PAMs like soil stabilization and infiltration enhancement in agriculture (Entry *et al*. 2008; Spofford and Pfeiffer 1996). Advances in theoretical chemistry have contributed to improvements in PAM performances through design of molecular conformations optimally suited to given industrial and environmental applications (Bicerano 1994; Bourani 1998; Bouranis *et al*. 1995; Chamberlain and Cole 1996). Nevertheless, many of the general principles from these studies are worth noting as a framework for understanding the environmental behavior of anionic high molecular weight PAMs. Additionally a good deal of information on the effects of coagulants and flocculants comes from the wastewater treatment literature, although often from polymers and compounds other than PAM, or in the case of PAM, often from cationic or nonionic formulations.

Mechanisms of PAM-based flocculants adsorption on mineral particles

The adsorption of PAMs from aqueous media onto mineral surfaces has been largely described in the literature. For instance the adsorption of PAM on soil and clay mineral surfaces has been demonstrated to be rapid and irreversible in several studies although the degree of adsorption itself is dependent on PAM conformation, soil or mineral properties, and soil solutions characteristics (Hollander *et al*. 1981; Nabzar *et al*. 1984; Nabzar *et al*. 1984; Nabzar *et al*. 1988; Nadler *et al*. 1992; Pradip and Fuerstna 1980; Tanaka *et al*. 1990; Stutzmann and Siffert 1977; Theng 1982; Tekin *et al*. 2005, Tekin *et al*. 2006; Deng *et al*. 2006; Tekin *et al*. 2010). As PAM adsorption implies multi-segment interactions, there is a small probability that all train segments are simultaneously detached from the surface (Theng 1982). Once adsorbed, less than 3% of the adsorbed PAM is removed from clay minerals after four consecutive washes (Deng *et al* 2006). Moreover according to Nadler *et al.* (1992), after adsorption and drying, little desorption of anionic PAM from soil occurs. Michaels and Morelos (1955) reported that 20% hydrolysis of PAM provided the greatest degree of chain extension,

150 facilitating its adsorption. As PAMs are drawn to mineral particle surfaces, surface-adsorbed water is
151 driven away because of the stronger attraction for the polymer (Parfitt and Greenland 1970). Sorption
152 isotherms of PAM generally fit with the linear form of Langmuir equation in comparison with the
153 Freundlich isotherm (Lu *et al*. 2002; Deng *et al*. 2006; Tekin *et al.* 2005; Tekin *et al*. 2006; Tekin *et al*.
154 2010). Additionally results of sorption experiments and parameters of Langmuir isotherm found in early
155 studies are consistent with a favorable adsorption and a high affinity of PAM to soil minerals. This high
156 affinity is likely due to the mechanisms of multi-segment sorption of the long chain of PAM (Theng
157 1982).
158 Stutzmann and Siffert (1977) showed that the fixation mechanism of partly hydrolyzed PAM onto clays
159 in a weakly acidic media is a chemisorption phenomenon. The anionic polyelectrolyte is in fact sorbed
160 exclusively on the external surface of the clay, where organic molecules undergo protonation and are
161 retained by ionic interaction. Charge transfer apparently depends on the polarizing power of the
162 exchangeable cation of the clay and a linear relationship was found between the polarizing power of
163 the alkali elements and the quantity of material sorbed.
164 Hydrogen bonds are thought as the main mechanism of adsorption of polymers on mineral surfaces.
165 Adsorption studies of clay-organic complexes have shown that two kinds of H-bonding are possible.
166 One type of H-bonding can occur between the amide groups of PAMs and the protonated aluminol
167 groups on the edge of clays (Laird 1997). Depending on pH value, amide group of the PAM can
168 adsorb either on silanol anchoring sites (at pH 4) or on aluminol anchoring sites (at pH 10) (Pefferkor
169 1987). Another type of H-bonding was proposed between carbonyl groups and edge aluminols (Laird
170 1997). Infrared analysis of clay-organic complexes has shown H-bonding between amide groups of
171 PAM and water molecules in the hydration shell of exchangeable cations of a smectite (Deng *et al*.
172 2006). Finally, ion-dipole interaction has been proposed in controlling the adsorption of PAM on
173 smectite. This interaction takes place between exchangeable cations of smectite and the carbonyl
174 oxygens of amide groups ($CONH_2$) of PAM (Deng *et al*. 2006).
175 For anionic PAMs, adsorption on kaolinite, illite and quartz is enhanced in the presence of divalent
176 cations through a cationic bridge process. Cationic bridges take place between divalent cations and
177 negative groups of anionic polymer on one hand and divalent cations and negatives sites of mineral
178 surfaces on the other hand. This binding mode occurs at high concentrations of divalent cations (Ca^{2+},

179 Mg^{2+}), and enhances the sorption of anionic polymers on negative mineral surfaces (Theng 1982
180 Chiappa *et al.* 1999).
181 Adsorption of PAMs on the mineral fraction is correlated with size of particles. Clays being the mineral
182 components with the lowest size have more affinity for PAMs than larger particles like sand and silt (Lu
183 *et al*. 2002; Gravelieng *et al*. 1997; Malik and Letey 1991). Clays with a high specific outer-surface
184 area such as montmorillonite and smectite are better PAMs adsorbents than clays with low specific
185 outer-surface areas such as kaolinite and illite (Lu *et al*. 2002; Deng *et al*. 2006; Inyang and Bae
186 2005). Additionally the charge repulsions confer to anionic PAM coil an extended conformation making
187 difficult its entry in the interlayer space of clay minerals (Stuzmann and Siffert 1977). Nevertheless, a
188 small amount of PAM molecules has been shown to penetrate in the interlayer space of
189 montmorillonite due to its large interlayer space (Inyang and Bae 2005). It was also shown that
190 adsorption of PAM increased on montmorillonite when the degree of hydrolysis of PAM increased.
191 PAM indeed tends to take the conformation of an extended chain when it is highly hydrolyzed.
192 Therefore the adsorption of PAM depends on the configuration and the volume of the solvated
193 macromolecule (Stuzmann and Siffert 1977). In contrast, a change of molecular weight has practically
194 no influence upon the adsorption ratio.
195
196 ***Physico-chemical parameters influencing the adsorption of PAM: pH, ionic strength and***
197 ***temperature***
198
199 The pH value influences both the structure of adsorbent, adsorbate and adsorption mechanism of
200 PAMs on solid surfaces. The effect of pH on the polymer consists on load changes of functional
201 groups by the phenomenon of protonation or deprotonation. At a high pH value, the carboxyl group (-
202 COOH) of polymer can be dissociated as follows: ($-COOH = -COO^- + H^+$), giving the polymer a
203 negative charge. Furthermore, amides groups can be hydrolyzed and generate carboxyl groups (-
204 $CONH_2$ = -COOH + COO^-) (Deng *et al.* 2006). The net charge of natural solids like clays and silicates
205 also depends on the pH. For instance the edge sites of aluminosilicates minerals are amphoteric
206 groups, able to fix or release protons. Thus, the surface charge can be positive when pH is inferior to
207 PZC (point of zero charge), neutral when pH is equal to PZC, or negative when pH is superior to PZC.
208 pH values inferior to the PZC induce the protonation of aluminol groups which confers to solid surfaces

a positive net charge. Inversely, at pH values superior to the PZC, aluminols sites and silanols sites are deprotonated, the surface charge becomes negative. Unlike cationic PAMs, the sorption of anionic PAMs is promoted when the surface is positively charged. This is mainly due to the reduction of electrostatic repulsions between negatives charges of polymers and the negative charges of the mineral surface. When pKa[COOH/COO^-] < pH < PZC, attraction of carboxylic groups towards aluminol groups is enhanced since PAM is negatively charged and the surface is positively charged. When pH > pKa[COOH/COO^-] and pH > PZC, the complete dissociation of carboxylic groups reinforces the negative charges of PAM and the surface is negatively charged. This results in the decrease of the adsorption of PAM (Lee *et al*. 1991). The adsorption of PAM tends toward zero when the pH value still increases because of the very large electrostatic repulsions and the sharp reduction of AlOH sites (Deng *et al*. 2006; Lee *et al*. 1991).

The ionic strength is also an important parameter. Benhur *et al.* (1992) found that the adsorption of PAMs onto illite and montmorillonite clays was generally in the order cationic > nonionic > anionic regardless of the electrolyte content of the solvating water. Water that was more saline and sodic reduced the adsorption of cationic and nonionic PAMs but increased adsorption of anionic PAMs. The results obtained in saline media may be explained by a size decrease of the PAM macromolecules, allowing a closer approach to the surface of the mineral substrate, and by a chain lengthening as the degree of hydrolysis increases, induced by the electrostatic repulsions between the COO^- groups of the medium. Aly and Letey (1988) found that the adsorption of anionic PAMs in water of electrical conductivity (EC) 0.7 dS m^{-1} was greater than for water of EC of 0.05 dS m^{-1}. Entropy change as water is displaced is an important actuating force in bringing about adsorption of negative and nonionic polymers to negatively charged clay surfaces (Lyklema and Fleer 1987; Theng 1982). As the adsorption of anionic PAMs on mineral surfaces is governed by the competition between polymer attractive interactions with solid surfaces and repulsive electrostatic forces (Lecourtier *et al*. 1990), the sorption of anionic polyacrylamide is increased when electrostatic repulsions are screened by cation bonding on the negatively charged surface sites (Lu *et al*. 2002; Lu and Wu 2003). It has also been demonstrated that the adsorption of anionic PAM on the edge surfaces of kaolinite is strongly dependent on salinity (Lee *et al*. 1991). Indeed, two effects have been reported. First, the adsorption of mono and divalent cations from the electrolyte on the negatively charged surface screens the

239 electrostatic repulsion between anionic PAM and the mineral surface. Secondary, since divalent
240 cations are involved in the cationic bridge the sorption saturation of PAM is higher in the presence of
241 divalent cations than in the presence of monovalent cations (Lu *et al*. 2002). Moreover cation
242 enhancement of sorption is more effective in fine-textured soils than in coarse-textured soils.
243
244 Finally, studies conducted on the effect of temperature on the adsorption of anionic PAM have shown
245 contradictory results. Increasing temperature (from 20°C to 60°C) was found to increase the
246 adsorption of anionic polyacrylamide on kaolinite, sepiolite and perlite (Mpofu *et al*. 2004; Tekin *et al*.
247 2005; Tekin *et al*. 2006; Tekin *et al*. 2010). This effect was attributed to two phenomena. Firsly,
248 increasing temperature results in a break of polymer-water hydrogen bonds that promotes the
249 polymer-polymer interactions. The polymer thus adopts a more compact conformation that will adsorb
250 more than the expanded one (Mpofu *et al*. 2004). Secondly, increasing temperature may produce a
251 swelling effect within the internal structure of the clay so the PAM can penetrate further (Tekin *et al*.
252 2005).
253

254 ### 3.2. PAM Transfer

255 ***Transfer in water***

256 Both molecular properties and product preparation can influence PAMs behavior in hydrosystems
257 (Callebaut *et al*. 1979). Results from monitoring of PAM concentrations in the drainage water of a
258 tunnel in Sweden where PAM was used showed that PAMs leaked out, both in connection with the
259 injection and in connection with after-injection using other grouting agents (Weideborg *et al*. 2001).
260

261 ***Flocculation***

262 The general principles of flocculation involving PAMs can be easily drawn from the abundant literature
263 dedicated to the adsorption of PAMs from aqueous media onto natural mineral surfaces (Greenlan
264 1963; Bottero and Lartiges 1992; Barvenik 1994; Theng 1979; Theng 1982; Sokja *et al*. 2007; Benhur
265 *et al*. 1992; Haschke *et al*. 2002; Lu *et al*. 2002; Lurie and Rebhun 1997). In an aqueous solution with
266 sufficient electrolytes, coulombic and van der Waals forces attract suspended particles to anionic
267 PAM. These surface attractions stabilize the structure of the aggregates by enhancing particle
268 cohesion. PAM efficiency as flocculants is not only due to adsorption phenomena. As can be seen on

Fig. 2, adsorbed PAM can present three different conformations: “train” conformation, “loop” conformation or “tail” conformation. Loops and tails can adsorb onto other particles enabling gathering of several particles in a process known as “polymer bridging”. This phenomenon increases with the molecular weight of PAMs.

The charge density plays also an important role in flocculation process. In anionic PAMs, carboxylic groups are distributed regularly on the molecular chain, which enhances the polymer extension by electrostatic repulsion. On another hand, those charges decrease the adsorption onto natural particles charged negatively (like clay particles). The use of PAMs poorly charged and with a high molecular weight usually decreases the competition between both phenomena and favor bridging processes. Small amounts of dissolved Ca^{2+} or Mg^{2+} can also help by shrinking the electrical double layer surrounding particles and bridging the anionic surfaces of particles and anionic PAM molecules. The mechanisms by which flocculation of suspended sediments takes place in the presence of polyelectrolytes was studied by Ruehrwein and Ward (1952) who associated this effect with stabilization of soil and resistance to dispersion. Benhur and Letey (1989) and Benhur *et al*. (1989) attributed this effect to the mechanism that reduced particle dispersion when sprinkler irrigating with PAM, which in turn reduced surface sealing and slowed the reduction of infiltration rate.

At temperatures from 6 to 29 °C, flocculation for a variety of inorganic and polymer compounds tended to be slower and flocs tend to be smaller than at higher temperatures (Fitzpatrick *et al*. 2004; Hanson and Cleasby 1990). Furthermore, floc strength seems to vary with the shear conditions of the flow media in which flocs are formed. Larger flocs formed at higher temperatures are more easily disrupted and less capable of reformation than flocs formed at lower temperatures (Fitzpatrick *et al*. 2004; Yeung and Pelton 1996; Yeung *et al*. 1997).

PAM solutions usually promote flocculation of suspended solids at low concentrations but can have the opposite effects at higher concentrations, where the large physical domain of the macromolecules themselves interfere with flocculation and actually stabilize dispersed suspensions as viscosity increases. When there is too much of PAM added in the suspension, a compression of the polymer can also be observed on the particle and there is not enough sites available for bridging, which decreases the flocculation efficiency. The concentration, at which the effects reverse, depends on several factors including PAM molecular weight, charge and conformation of the molecule, size and chemistry of the dispersed solids, and chemistry of the water, particularly its electrical conductivity

(Sato and Ruch 1980). The treatment of an effluent containing suspended particles requires determining precisely the optimal concentration of PAM which must be added in order to perform an efficient flocculation. This concentration is usually proportional to the particles concentration and is almost always below 1 $mg.L^{-1}$ of suspension.

Transfer with suspended matter

A study measured PAM concentrations in 167-m-long PAM-treated tail ditch that received this runoff (Lentz *et al*. 2002). The soil was a Portneuf silt loam (coarse-silty, mixed, superactive, mesic applications Durinodic Xeric Haplocalcid) with a 1.5% slope. PAM was adsorbed to soil and removed solution as the streams traversed the soil-lined channels. The removal application rate increased with the stream sediment concentration. Additionally a previous study reported that PAM applications of 1 to 2 $mg.L^{-1}$ controlled furrow erosion similarly on 1.5% sloping fields (Lentz and Sojka 2000). The linear PAM molecule assumes the form of a hydrated random coil when dissolved in water. Solvated PAM molecules in the furrow stream collide with soil particles when treated water infiltrates into soil or when turbulent flow drives the molecules against entrained sediment or the wetted soil perimeter. The dissolved high molecular weight polymers are in fact readily adsorbed to soil particles via electrostatic, hydrogen, and chemical bonding, and by displacement of inner solvation-sphere water molecules (LaMer and Healy 1963; Mortland 1970; Jin *et al*. 1987; Malik *et al*. 1991; Laird 1997). As a result, incoming PAM is bound to soil in the upper 1 to 5 cm of the profile (Malik *et al*. 1991). Dry soil adsorbs more polymers than wet soils because sorbed water reduces the number of potential soil binding sites (Chang *et al*. 1991). PAM is adsorbed to particulate matter and flocculates soils suspended in water. Polymer adsorption on soil occurs rapidly during the first minutes of exposure but may continue at a reduced rate for several hours or days (Van de Ven 1994). In batch tests (soil, water, and dissolved PAM mixed in a shaker), Nadler *et al*. (1992) reported that little or no polymer desorbed from the soil while it remained wet, and the polymer became irreversibly bonded to the soil upon drying. In flowing systems, Lee and Fuller (1985) found that polymer adsorption rate decreased with increasing velocity of flow. Polymer desorption did not occur under quiescent conditions but was observed when the adsorbent material was subjected to flow shear. Desorption increased with the increasing flow velocity. These authors also concluded that adsorbed PAMs do not penetrate soil aggregates, but only coat and stabilize their surfaces. Malik and Letey (1991) and Nadler and Letey (1989) used tritium-labeled

329 polymers to determine sorption isotherms of several types of polyanions on Arlington sandy loam
330 (coarse-loamy, mixed, thermic Haplic Durixeralfs). They interpreted their results as showing that
331 polymer sorption was restricted to the external surfaces of soil aggregates. A similar conclusion was
332 reached by ElHardy and Abd ElHardy (1989) who saw only limited intrusion of high molecular weight
333 PAMs into soil aggregates. Aly and Letey (1988) showed that the water quality of the solvating water
334 used to apply the polymers also greatly influenced the degree of adsorption.
335 Soils with a high clay or silt content, fine texture and low organic matter content had high sorptive
336 affinity for PAMs. According to Lu *et al*. (2002), organic matter decreased the amount of anionic PAM
337 adsorption on soil. The negative effect of organic matter on PAM sorption was attributed to the
338 reduction of accessible sorption sites by cementing inorganic soil components to form aggregates and
339 to the enhancement of electrostatic repulsion between PAM and soil surface by its negatively charged
340 functional groups. The length of the polymer chain and large number of adsorption sites along the
341 molecule contribute to PAM's adsorption always attached to the adsorption surface, preventing
342 removal of the molecule (Nadler and Letey 1989). Because of the demonstrated high sorptive ability
343 and low mobility (Malik and Letey 1991; Malik *et al*. 1991), PAM is generally regarded as incapable of
344 penetrating soil more than a few centimeters from the soil surface. This, considered in light of the
345 relatively slow sorption kinetics of the large PAM molecule (Lu *et al*. 2002), has led to recognition that
346 the depth of PAM penetration depends on PAM properties, application method, and the soil and water
347 properties present in the application scenario (Lu and Wu 2003). Using anionic PAMs of 10-15 mg
348 mol^{-1}, Lu and Wu (2003) found that PAM penetration depth was about one-eighth to one-half of the
349 water penetration depth, with a particularly high PAM retention in the top few centimeters of the soil.
350 The PAM retained in the top 0-2 mm of soil ranged from 16% to 95% of the total applied. PAM
351 retention was greater at shallow depths when solution contact with the soil was favored by pore
352 arrangement, contact time, and drier soil conditions on addition of PAM solutions.
353
354 **3.3. Transfer of AMD**

355 Mobility of AMD in soils has been little studied. Adsorption of AMD on kaolinite, montmorillonite and
356 anionic, cationic, and hydrophobic resins is insignificant (Brown *et al*. 1980), at acrylamide
357 concentrations between 500 µg L^{-1} and several mg L^{-1}. Arrowood (2008), who studied the adsorption
358 of acrylamide on different soils (silica sand, coarse sandy soil, loam soil) at AMD concentrations lower

than those tested by Brown *et al*. (1980), observed acrylamide adsorption on the three soils with better affinity for the clay one. The authors concluded that the adsorption of AMD was inversely proportional to initial concentrations of acrylamide and remains insignificant when compared to the ability of bacteria to breakdown acrylamide in natural environment. The low affinity of AMD to soil and clay minerals in particular is likely due to its high hydrosolubility and small size (Sojka *et al*. 2007). Analysis of a lake water, directly connected to groundwaters, suggest a likely transfer of AMD due to its infiltration in soils (Junqua *et al.* 2013). The half-life of acrylamide monomer in rivers ranges from weeks to months (Brown *et al.* 1980).

4. Degradation of PAM-based flocculants

4.1. Mechanisms of PAM degradation

PAM-based flocculants degradation has been mainly studied for PAMs in aqueous solutions. The degradation of PAMs results in a reduction of the molecular weight of the polymer and can adversely affect the performance of such aqueous solutions in their commercial application as flocculants. Degradation involving chain scission is accompanied by a significant change in the rheological properties of the polymer solutions and this has often been used to monitor and express the extent of the degradation. A correlation between the reduction in solution viscosity and performance as a flocculating agent has been demonstrated in number of references. However the factors leading to such degradation and the mechanisms of the degradation processes are not completely elucidated.

In environmental applications (such as in flocculation processes), very few experiments have been conducted to quantify the PAM degradation in natural hydrosystems. Some reports have indicated that polyacrylamide, in the presence of sunlight and glyphosate, photolytically degrades to acrylamide monomer and this is a direct introduction of acrylamide into agricultural areas (Smith and Oehme 1993, Smith *et al*. 1996; Smith *et al*. 1997). The main difficulty encountered is due to the lack of simple methods to analyze and quantify PAM in this context. Thus what is known about PAM degradation is drawn from sparse reports, often using smaller molecular weight PAMs, or from indirect measurement of decomposition. Most studies report slow degradation rates as a result of mechanical, photochemical and biological processes.

Mechanical degradation

Aqueous solutions of PAM or floc suspensions can both undergo mechanical degradation due to a variety of processes such as stirring, pumping, injection and movement through porous media and direct mechanical load. In the aggregate treatment plant, mechanical degradation of the PAM can occur due to a shearing hydrodynamic field (mixing of the PAM-based flocculants with the process waters and transportation of the sludge to tailings ponds along pipelines through pumping) or by direct mechanical load (solid/liquid separation and sludge dewatering with a press-filter).

It was reported that a shearing hydrodynamic field induced chain bond scissions leading to a decrease in the molecular weight of the polyacrylamide and then to a decrease in intrinsic viscosity of PAM solutions (Paterson and Abernathy 1970; Abdel-Alim and Hamielec 1973; Nagashiro *et al.* 1975; Povkh and Chernyuk 1986; Nguyen and Boger 1998; Avadiar *et al.* 2013). In particular, mechanical degradation of polymers used for drag reduction in a turbulently flowing liquid has been studied by several authors (Rho *et al.* 1996; Vlachogiannis *et al.* 2003; Pereira and Soares 2012). Losses in the effectiveness of the polymers in reducing drag under flow were attributed either to fractures of the PAM molecules leading to changes in the molecular weight distribution or to the fact that some or all of the degradation could be associated with a decrease of aggregation in a shear flow (Wade and Kumar 1972; Vlachogiannis *et al.* 2003).

Regarding mechanical degradation of flocs, Tang *et al*. (2001) showed that the mechanical strength of the floc depends on both the interparticle forces and on the floc density. In general, the rupture of floc is classified either as “surface erosion” or as “large-scale fragmentation” (Yeung and Pelton 1996). Erosion is the separation of small particles from the floc surface and it is attributed to shearing stresses on the floc surface. Floc breakage during shear is suspected to involve the rupture of hydrogen bonds (Senden *et al.* 2000; Taylor *et al.* 2002). Fragmentation refers to the break-up of flocs into pieces of comparable size caused by pressure gradients across the entire body. Since flocs break-up occurs at the weakest point in the floc structure, this usually results in more compact aggregates, though smaller than the initial flocs. According to Caulfield (2002), it cannot be stated that under the influence of a mechanical load polyacrylamides degrade to form their constituent monomeric units such as acrylamide. Moreover, several authors reported that the flocs formed using polyelectrolytes such as PAM are reformed after being broken up but do not regain their original size and structure and form a new structure more compacted (Nguyen and Boger 1985; Leong *et al.* 1987;

419 Spicer *et al.* 1998). An example of experiments on mechanical degradation was performed by Rasteiro
420 (2008) who studied the degradation under hydrodynamic shearing induced by a recirculating pump of
421 two high molecular weight cationic PAMs used for the flocculation of precipitated calcium carbonate.
422 For the pump speeds tested, the flocs size decrease was attributed to floc erosion but it was also
423 stated that flocs reach another equilibrium state where aggregation and fragmentation rates are the
424 same. Moreover, it was reported that erosion may not depend on the flocculant concentration since it
425 depends on the interparticles bonds of the flocs; however erosion increased with the pump speed.
426 Reflocculation occured only for the higher flocculant concentrations due to the excess of polymer and
427 most of the flocs resulting from the reflocculation process were observed to be more compact than the
428 original ones Rasteiro (2008).
429 Mechanical load can also induce enough shear-induced stress to cause bond scission and the
430 formation of a macromolecular radical (Caulfield 2002). For example, it was observed that filtration
431 under pressure of thickened suspensions from PAM flocculation of bauxite residue or brown coal lead
432 to significant breakdown in network structures and reduction in yield stresses (Nguyen and Boger
433 1985; Leong *et al.* 1987). The implementation of shear stresses that are higher than the initial yield
434 stresses of flocs suspension leads then to breakdown the intricacy involved within these complex
435 network structures (Avadiar *et al.* 2013).
436 Therefore, mechanical degradation of aqueous solutions of PAM or floc suspensions often involves
437 irreversible changes of the polymeric material including a marked reduction in viscosity and a scission
438 of the main chain bond and thus the generation of free radicals. However, none of the studies found in
439 the literature suggest that PAMs degrade to AMD under mechanical constraints.
440
441 ***Photodegradation of polyacrylamide***
442 PAM photodegradation is reported to be a free radical process that can lead to a cleavage of the
443 polymer backbone (bond scission) and the formation of lower molecular weight products (Decker
444 1989; Caulfield *et al*. 2002). The C-C, C-H and C-NH bonds in PAMs have bond strengths of 340, 420
445 and 414 kJ mol^{-1} which can be cleaved by wavelengths of 325, 288 and 250 nm respectively (Crosby
446 1976). Even if the atmosphere absorbs most of the lower spectrum (less than approximately 300 nm),
447 it still leaves components from the UV and visible regions with sufficient energy to disrupt chemical
448 bonds (Rabek 1996). The free radicals formed from bond scission are extremely unstable and will

449 react with any suitable substrate. The reactions include combination to reform the saturated carbon-
450 carbon polymer backbone, disproportionation to form an unsaturated and saturated polymer chain end
451 and reaction with other entities present. The presence of oxygen in the system has a strong impact on
452 photodegradation of PAM as well as the impurities contained in the initial polymer.
453 Some authors have studied PAM degradation via advanced oxidation processes, such as Fenton
454 (Kurenkov *et al*. 2002), H_2O_2/UV (Caufield *et al*. 2002), photo-Fenton (Giroto *et al*. 2008) and
455 O_3/H_2O_2/UV (Ren *et al*. 2006), but these reactions cannot occur in environmental conditions.
456 Most of the studies, dedicated to PAM photodegradation in environmental conditions, focus on the
457 potential release of AMD. This phenomenon was firstly observed by Smith *et al. (*1996, 1997), in
458 controlled laboratory conditions and under environmental conditions using an aqueous solution of a
459 PAM thickening agent (PAM mixed with glyphosate). However these results, their interpretation and
460 the overall experimental design raised some controversy, particularly the way that PAM was prepared
461 which could lead to incomplete dissolution of PAM (Kay-Schoemake *et al*. 1998a; Ver Vers 1999;
462 Caulfield *et al*. 2002). Ver Vers (1999) reported work using analogous degradation conditions but
463 yielding different results. This study points out problems in proper dilution of the emulsion and
464 attributes the detection of small amount of AMD over time to the gradual release of unreacted AMD
465 contaminants from the incompletely dissolved emulsion. The author concluded that PAM does not
466 degrade to AMD monomer in the presence of sunlight, even in presence of glyphosate. Kay-
467 Shoemake *et al*. (1998b) showed that the treatment of solutions of high molecular weight anionic
468 PAMs with UV radiations reduced the PAM chain length. They found also that the photodegraded
469 PAM samples did not support bacterial growth as sole source of carbon. As it is well recognized that
470 acrylamide is completely biodegradable (see section VI), these results suggest that AMD is not formed
471 during the photodegradation of the polyacrylamide. El-Mamouni *et al*. (2002) investigated the
472 photodegradation of a PAM solution (PAMs molecular weight ranging between 10^5 and 10^6 daltons)
473 exposed to UV irradiation (254 nm) prior to biomineralization. They observed a shift in the molecular
474 weight distribution, which demonstrates the degradation of the PAM chains into oligomers. A study
475 leaded by Caulfield *et al*. (2003) has reported that strong UV radiation at 254 nm released AMD from
476 solutions of a nonionic PAM. However, the release was very small. They also noted a reduction in
477 viscosity of the polymer solution, attributed to a lowering of the molecular weight consistent with
478 polymer chain scission. Suzuki *et al*. (1978, 1979) also reported a number of low molecular weight

PAM decomposition products when degraded using strong UV irradiation in the presence of ozone but didn't notice any AMD monomer release. It must be noted that the studies of Kay-Schoemake *et al*. (1998a), El Mamouni *et al*. (2002), Caulfield *et al*. (2003) and Suzuki *et al*. (1978, 1979) used UV irradiations which are much more energetic than the sunlight's wavelengths. These studies cannot confirm the attenuation of PAM by sunlight in natural environments.

Holliman *et al*. (2005) submitted samples of field-conditioned cross-linked PAM gels to a 365-nm UV radiation in a daily light-dark cycle during 5 months without detectable acrylamide release. On the other hand, they observed a gradual loss of gel properties they attribute to polymer chain scission resulting in the production of PAM fragments. More recently, a study by Woodrow *et al*. (2008) reportedAMD release resulting from sunlight irradiation of aqueous polyacrylamide/iron mixtures. A solution of commercial anionic PAM with different concentration of Fe^{3+} (from 0.02 to 4.4 ppm) was submitted to UV irradiation in a simulator able to closely approximate solar irradiance in the troposphere (equivalent to late summer noontime sunlight at 40° latitude – 300nm). Without Fe^{3+}, only polymer chain scission was observed through HPLC measurement and decline of average molecular weight. In the presence of Fe^{3+}, acrylamide release was also observed at acid/neutral pH whereas at alkaline pH (~ 8.0), PAM/Fe^{3+} remained stable under irradiation.

In conclusion, PAMs are susceptible to a wide range of photodegradative processes depending on the reaction conditions. Photodegradation results in irreversible changes in both physical and chemical properties of the PAMs, but the release of acrylamide still remains in question and would require further clarification. Moreover photodegradation of PAM was not directly demonstrated in environmental conditions in hydrosystems with field studies but only in laboratory aqueous solutions without the presence of mineral particles.

Biological degradation

Whether they are used as flocculants for water clarification or in agricultural applications for the control of soil erosion as well as in petrochemical productions to enhanced oil recovery, PAMs are in contact with micro-organisms and can be subject to biodegradation. Most of the studies on the degradation of PAM in agricultural soils concluded that the biodegradation of PAM did not result in the formation of monomer (AMD) and that PAMs were generally resistant to microbial degradation (Caulfield *et al*.

508 2002). During these applications, the degradation seemed to be most likely due to environmental
509 factors such as UV light or chemical degradation (Seybold 1994).
510 The ability of bacteria to utilize PAM as sole nitrogen or sole carbon sources has been examined. Kay-
511 Shoemake *et al.* (1998a) demonstrated that PAM can be used as an organic nitrogen source for
512 microorganisms in soil. A bacterial growth was observed when cultures were produced on soil
513 samples with no other source of nitrogen. Intracellular and extracellular amidase activities were
514 detected in all the enrichment cultures able to use PAM as sole source of nitrogen and in soils treated
515 with PAM. Haveroen *et al.* (2005) also demonstrated that the addition of PAM stimulates microbial
516 activities and methanogenesis in anaerobic environments that are poor in nitrogen sources. In another
517 study, Kay-Shoemake *et al.* (1998b) show that indigenous bacteria, commonly found in soils, were
518 enabled to used PAM as sole carbon source. These results suggest that these microorganisms could
519 hydrolyse the amine group but were enable of cleaving the main carbon chain of the polymer.
520 PAMs are high molecular weight polymers and are unable to pass biological membranes, so the
521 biodegradation of these polymers requires the action of extracellular enzymes, like amidases, to
522 degrade the carbon chain. These characteristics limit the potential of biodegradation and can be at the
523 origin of the partial degradation of PAM (Caulfield *et al.* 2002). Few studies demonstrated the
524 biodegradation of these compounds. Nakamiya and Kinoshita (1995) were the first ones to report the
525 isolation of two PAM-degrading bacterial strains from soil samples. These strains, identified as
526 *Enterobacter agglomerans* A and *Azomonas macrocytogenes* B, were able to reduce the molecular
527 weight of a synthesized PAM and to degrade about 15 to 20% of the initial concentration of PAM in a
528 synthetic medium. Another study (Matsuoka *et al.* 2002) reported the isolation of two PAM-degrading
529 bacteria strains from soil, identified as *Bacillus sphaericus* n°2 and *Acinetobacter sp.* No. 11. These
530 strains grew on medium containing PAM as sole carbon and nitrogen sources and reduced,
531 respectively, by 16% and 19% of the initial PAM concentration. However, the degradation of PAM did
532 not result in the formation of AMD. As previously indicated, the biodegradation of PAM require
533 extracellular amidase activities. These enzymes seem to be enabled to liberate AMD directly from
534 PAM but can produce lower molecular weight polymers and can alter the nature of the substituents
535 attached to the polymer backbone (Caulfield *et al.* 2002, Kay-Shoemake *et al.* 1998b).
536 More recently, several bacterial strains isolated during oil recovery process have demonstrated the
537 ability to degrade Hydrolysed Polyacrylamide (HPAM) or PAM (Ma *et al.* 2010; Wen *et al.* 2010; Bao *et*

538 *al.* 2010). Ma *et al.* (2010) have isolated a *Clostridium bifermentans* H1 strain which can use HPMA as
539 sole carbon source and can hydrolyse the amine to carboxyl group by the molecule chain amine
540 hydrolysis. In their experimental conditions, the removing efficiency for HPAM reached 30.8 %. Wen *et*
541 *al.* (2010) reported the isolation of two strains of *Bacillus cereus* HWBI and *Bacillus flexu* HWBII from
542 activated sludge and oil-contaminated soil. Both strains were able to grow on a medium containing
543 PAM as sole carbon and nitrogen source and to degrade PAM at different rates. After 72 hours of
544 cultivation in a mineral salt medium (MSM) supplemented with 60 $mg.L^{-1}$ of PAM at 30°C, more than
545 70 % of the PAM was consumed and PAM was cleaved into smaller molecules. Another study
546 reported the isolation of two *Bacillus sp.* strains, named PM-2 and PM-3 from production water after
547 polymer flooding in an oilfield (Bao *et al.* 2010). The PAM removal efficiencies observed were lower
548 than others studies. After 7 days of cultivation at 40°C in a basal medium containing 0.5 $g.L^{-1}$ of HPMA
549 as a sole source of nitrogen, 36.3 % of the HPMA was degraded. Lower HPMA removal efficiencies
550 were observed when HPMA was used as sole carbon and nitrogen sources. These results suggested
551 that the PAM-degrading strains obtained more nutriments from the amide sides groups of HPAM using
552 amidase activities compared to cleaving the main carbon chain backbone (Kay-Shoemake *et al.*
553 1998b).
554 Although the biodegradation of PAM has been studied with isolated strains in pure culture, in practical
555 work, the biodegradation of PAM requires interactions between several microbial species. Recently,
556 Liu *et al.* (2012) have described a PAM-degrading granular sludge which degraded PAM. The PAM-
557 degrading granules which were mostly composed by filamentous and bacilli bacteria used PAM as
558 sole carbon and nitrogen source and degrade PAM at a high rate. PAM concentration was decreased
559 from 66.7 $mg.L^{-1}$ to 32.9 $mg.L^{-1}$ in 24 hours but no AMD monomer was detected during the
560 biodegradation process. The main intermediate product was identified as polyacrylic acid with a low
561 molecular weight.
562 These studies presented in this review demonstrated that PAM can be subjected to microbial
563 degradation. PAM was principally used as a nitrogen source by hydrolysis of the amine groups from
564 the polymer. The presence of glucose at low concentrations which can be used as co-metabolism
565 substrate can improve the PAM degradation but the biodegradation efficiency seems to be affected by
566 the initial concentration of PAM (Wen *et al.* 2010). The biodegradation of PAM induced changes in the
567 structure of the polymer (reduction of the molecular weight) but no evidence of release of AMD

monomer has been found. Although amidases are involved in the mechanism of degradation of PAM, the reaction pathway for the microbial degradation of PAM is not clearly identified.

4.2. Mechanisms of acrylamide degradation

Bio-degradation of acrylamide

AMD has an inhibitory effect on sulfhydryl proteins and hence on growth of microorganisms (Cavins and Friedman 1968). However, some microorganisms are able to grow in the presence of AMD and degrade this molecule. The microbial degradation of AMD has been demonstrated for several decades in studies investigating the behavior, fate and impacts of AMD in natural environments amended with PAMs. Microbial degradation was shown to occur in soils (Shanker *et al.* 1990, Shukor *et al.* 2009a), sediments (Labahn *et al.* 2010), wastewater (Buranasilp and Charoenpanich 2011, Nawaz *et al.* 1996) and hydrosystems (Labahn *et al.* 2010) and is mediated by microorganisms commonly presents in these environments. Most studies deal with the biodegradation of AMD by bacteria but some fungi have also been shown to degrade AMD. In particular, filamentus fungi such as some strains of *Aspergillus oryzae* have interesting AMD degradation ability (Wakaizumi *et al.* 2009).

Among bacteria having an AMD degrading ability, most documented belong to species within the genera *Bacillus* (Shukor *et al.*, 2009a), *Pseudomonas* (Labahn *et al.* 2010, Sathesh Prabu and Thatheyus 2007, Shanker *et al.* 1990, Shukor *et al.* 2009b) and *Rhodococcus* (Nawaz *et al.* 1998). However it is now establish that this activity is more widespread among bacteria such as *Enterobacter aerogenes* (Buranasilp and Charoenpanich 2011), *Enterococcus faecalis* (Buranasilp and Charoenpanich 2011) *Klebsiella pneumoniae* (Nawaz *et al.* 1996), Burkholderia sp. , *Xanthomonas maltophilia* (Nawaz *et al.* 1993), *Kluyvera georgiana* (Thanyacharoen *et al.* 2012), *Variovorax boronicumulans* (Liu ZH. *et al.* 2013), *Geobacillus thermoglucosidasius* (Cha and Chambliss 2013), *Ralstonia eutropha* (Cha and Chambliss 2011) or *Arthrobacter* strains (Yamada *et al*. 1979). The concentration of AMD that can be tolerated and degraded depends on the bacterial strain. As an example and among strains that tolerate the higher concentration of AMD, *Bacillus cereus* is able to degrade and assimilate AMD at concentrations as high as 3 g. L^{-1} (Shukor *et al.* 2009a). Shanker *et al.* (1990) isolated a *Pseudomonas sp*. strain able to degrade 4 g. L^{-1} AMD, and Enterobacter aerogenes was shown to grew well in the presence of 5 g. L^{-1} AMD (Buranasilp and Charoenpanich 2011). It has also been demonstrated that bacteria able to degrade AMD are also able to degrade

598 other aliphatic amides such as acetamide, urea, propionamide (Buranasilp and Charoenpanich 2011;
599 Shukor *et al*. 2009a).
600 The biodegradation of AMD was first shown to be aerobic but recent studies have demonstrated the
601 involvement of some bacteria in the anaerobic biodegradation of AMD. In particular, nitrate reducers
602 have been shown to significantly remove AMD (Labahn *et al*. 2010). These authors also demonstrated
603 the potential of sulfate- and iron-reducers to degrade AMD. The biodegradation of AMD leads to the
604 production of acrylic acid (AA) and ammonia (NH_3). This could explain that AMD degrading
605 microorgansims use AMD as nitrogen source and sometimes also as carbon source, and that some
606 bacteria can grow as AMD as the sole sources of N and C (Shukor *et al*. 2009a, Nawaz *et al*. 1994,
607 1996). From an experimental point of view, AMD can be analyzed directly either by HPLC or by UPLC
608 depending on the concentration (Togola *et al.*, 2014; Guezennec *et al.*, 2014; Touze *et al.*, 2014;
609 VerVers, 1999). The degradation of AMD can also be easily monitored by the quantification of
610 ammonia that can be achieved using indicator such as Phenol red that changes in color (from red to
611 pink) in the presence of ammonia (Santoshkumar *et al*. 2010).
612 Many studies also underlined that the AMD biodegradation activity of free cells and immobilized cells
613 can be different. It is in fact usually admitted that immobilized bacterial technology offers several
614 advantages over the application of free cells in the degradations of pollutants (Nawaz *et al*. 1998):
615 immobilized cells are known to retain high catabolic activity, can be reused, efficiently mineralize
616 substrates and offers physical protection from predators and parasites. Nawaz *et al*. (1998) thus
617 demonstrated that immobilized cells of *Rhodococcus sp*. rapidly degraded 64 and 128 mM AMD in 3
618 and 5 hours respectively whereas free cells took more than 24 h to degrade 64 mM AMD. Moreover
619 an AMD concentration of 128 mM inhibited the growth of the free cells. Sathesh Prabu and Thatheyus
620 (2007) observed that free *Pseudmonas aeruginosa* cells began the degradative activity of AMD only
621 after incubation of 24 h, while immobilized cells started before 24 h. On the opposite, Buranasilp and
622 Charoenpanich (2011) showed that AMD degradation by immobilized cells of *Enterobacter aerogenes*
623 was slower than that of free cells. This could be explained by an inappropriate immobilization process
624 or difficulties in substrate-cell contact.
625 In addition to the state (free or immobilized) of cells, the biodegradation of AMD is influenced by
626 several physical factors such as AMD concentration, temperature, pH, the presence of metals. Nawaz
627 *et al*. (1998) demonstrated that the biodegradation of *Rhodococcus sp*. was lower at low temperature

628 (less than 60% of AMD was degraded at 10°C in 4 h whereas 100 % of AMD was degraded in less
629 than 3 h at 28°C and 45°C). An incubation temperature of 55°C completely inhibited the degradation of
630 AMD by this strain. pH 7 favored maximum degradation of AMD, and activity was slower at pH 8 and
631 very little degradation was measured at pH 6. These authors also demonstrated that nickel and cobalt
632 slowed the AMD degradation ability (when used at 5 mM) or inhibit (when used at 10 mM) the AMD
633 degradation ability. The highest rate of degradation of AMD was observed in the presence of iron but
634 iron concentrations higher than 10 mM inhibited AMD degradation. Sathesh Prabu and Thatheyus
635 (2007) showed that mercury and chromium inhibited AMD degradation by *Pseudomonas aeruginosa*
636 while nickel enhanced the process.
637
638 ***AMD biodegradation in environmental conditions***
639 If numerous authors have investigated the mechanisms of AMD biodegradation and the
640 microorganisms involved, very few have quantified AMD biodegradation rate and kinetics in
641 environmental conditions (temperature, AMD concentration, natural samples…). Those study exhibit
642 contrasting results (see Table 1) and are difficult to compare since most of biodegradation tests have
643 been conducted in various range of AMD concentration. The work carried out by Labahn *et al*. (2010)
644 on natural water and slurry samples spiked with 50 $\mu g.L^{-1}$ AMD show the impact of the temperature on
645 AMD biodegradation: at 15°C, no degradation is detected after 72h whereas at 25°C, AMD
646 degradation is complete after 24h. These results confirm those obtained by Nawaz *et al*. (1998) in
647 controlled laboratory biodegradation study using pure strain of *Rhodococcus* sp (see section above).
648 Croll (1974) investigated AMD biodegradation in river water samples spiked with 10 $\mu g.L^{-1}$ AMD. One
649 of the water samples was inoculated with a culture capable of degrading acrylamide. In this case,
650 AMD degradation was complete after 50h, the lag period being 5h. In water samples which were not
651 inoculated, the time required to fully degrade AMD reached more than 300h with a lag period of 50h.
652 Brown (1979) used also river water samples but with higher concentration of AMD (5 $mg.L^{-1}$) and
653 investigated the influence of light on the biodegradation. In both cases (with and without light), the
654 results were the same: AMD was fully degraded after 125h with a lag time of 75h. In a more recent
655 study Ver Vers (1999) demonstrated that the time required for complete AMD biodegradation could
656 vary from 480h to more than 1100h according to the type of water samples (tap, river and lake). For

the author, those differences could indicate that some species in the water may be interacting with AMD, either accelerating or hindering monomer degradation.

The results obtained by these author show that AMD biodegradation is probably influenced by different types of factors such as the initial AMD concentration, the nature of the media in which the degradation occurs, its microbial composition… Given the conditions used, the degradation can be quick but the time required for a complete degradation of AMD is never lower than 1 day. In some cases several days are needed to degrade the monomer.

Metabolism of acrylamide and enzymes involved in bio-degradation

As mentioned before, AMD can be degraded by microorganisms under aerobic and anaerobic condition, and serves as nitrogen and/or carbon sources. Despite the fact that microbial degradation of acrylamide has been explored extensively, the metabolic pathways of degradation are unclear. The microbial degradation of AMD is initially due to the presence of an enzyme named acylamide amidohydrolase (E.C. 3.5.1.4) or amidase. Amidases catalyze the hydrolysis of an amide to free carboxylic acids and free ammonium. In the case of acrylamide, the AMD is deaminated to ammonia and acrylic acid (AA). These enzymes belong to the family of hydrolases which acts on carbon-nitrogen bonds other than peptide bonds. They are ubiquitous enzymes that can have various biological functions and the substrate preferences differ. In their review, Sharma *et al*. (2009) widely described these enzymes, their uses in industries (and their potential applications in the production of various chemicals), their structural and biochemical properties, substrates and some purification protocols.

Amidase activity has been identified in various bacteria genus, commonly found in soils, including *Rhodococcus*, *Bacillus*, *Brevibacterium*, *Alcaligenes* and *Pseudomonas* and in fungi (Kay-Shoemake *et al*. 1998b, Wakaizumi *et al*. 2009). These micro-organisms are able to produce a single amidase or numerous isoenzymes during growth with amide substrate. Furthermore, amidases exhibited enzymatic activity with relatively limited substrate specificity while others are able to hydrolysis a broad range of spectrum. Among amidases, some have been demonstrated to be involved in the first step of the AMD-degrading microbial pathways for the catalytic hydrolysis of AMD to acrylic acid and ammonia (Sharma *et al*. 2009).

686 Although some amidases are constitutive (Nawaz *et al*. 1994), microbial amidases are generally
687 inducible. It has been demonstrated that amides and AMD can be an inducer of amidase expression
688 and some carbon sources as glucose or succinate can induce a catabolic repression (Potts and Clarke
689 1976, Sharma *et al*. 2009). The regulation of amidase (encoded by *amiE* gene) expression has been
690 study in *Pseudomonas aeruginosa*. In this microorganism, the induction of amidase synthesis is
691 positively regulated by a regulatory protein encoded by *amiR* and a second regulatory gene, *amiC*,
692 which negatively regulates amidase expression (Clarke *et al*. 1981, Cousens *et al*. 1987, Wilson. and
693 Drew 1991, Wilson *et al*. 1993, Wilson and Drew 1995). However, under non-inducing condition, low
694 levels of amidase activity are always present within the cells. But, the cellular mechanism for induction
695 or sensing remains unclear because the PAM-polymer is too large to enter the cells and to act as a
696 direct inducer. Shanker *et al.* (1990) have demonstrated that addition of glutamate or ammonium
697 sulfate as additional nitrogen source induced increase in degradation potential.
698 Several amidases using AMD as substrate have been purified from AMD-degrading bacteria (Cha and
699 Chambliss 2013; Egorova *et al*. 2004; Lavrov *et al*. 2010; Liu *et al*. 2013; Makhongela *et al*. 2007;
700 Nawaz *et al*. 1994; Nawaz *et al*. 1996; Ohtaki *et al*. 2010; Syed *et al*. 2012). The amidases purified
701 from AMD-degrading bacteria are mainly monomer but that from *Burkholderia sp*. is a homotetramer
702 (Syed *et al*. 2012). The molecular weight, pH and temperature optima depend on the enzyme (see
703 Table 2). It has been also demonstrated that the catalytic hydrolysis of AMD by amidase can be
704 inhibited or enhanced by metals (Nawaz *et al*. 1994). These authors showed that amidase activity of
705 *Rhodococcus sp*. was enhanced by Fe^{2+}, Ba^{2+} and Cr^{2+} but not dependent on these cations. On the
706 other side, the enzyme activity was partially inhibited by Mg^{2+} and totally inhibited in the presence of
707 Ni^{2+}, Hg^{2+}, Cu^{2+} and Co^{2+}.
708 The biodegradation of AMD requires not only amidase but also enzymes able to metabolize the
709 intermediate products. Indeed, the biodegradation of AMD induces the production of ammonia and
710 acrylic acid. However, the subsequent fate of these products is not clear but probably involves specific
711 catabolic pathways. For AMD degrading-bacteria, AA is probably reduced to generate energy for
712 bacterial growth but the catabolic pathway is not clear. Wampler and Ensign (2005) suggested that AA
713 is degraded to β-hydropropionate via hydroxylation reaction, then oxidized to CO_2 or reduced to
714 propionic acid. Recently, Charoenpanich and Tani (2014) have studied the response of an acrylamide-
715 degrader *Enterococcus aerogenes* to AMD using proteome analysis. These authors have identified

fifteen proteins differentially expressed after growth in presence of AMD and have proposed a model of metabolic pathway of AMD degradation based on these results (see Fig. 3).

Finally, the identification of a “universal” pathway and the enzymes involved in AMD metabolism in prokaryotes remains a challenge for the optimization of the bioremediation of AMD.

5. Conclusion

This review summarizes the literature which gives information and scientific data on the fate of PAM-based flocculants in hydrosystems. PAM and associated AMD have been considered and three main families of phenomenon have been investigated: transport, adsorption and degradation. Most of the information gathered in this review was derived from studies conducted in the frame of PAM use for agricultural application. Due to PAM ability to adsorb onto mineral particles, its transport in surface water, groundwater and soils is rather limited and restricted to specific conditions. PAM adsorption is rapid and irreversible, and desorption occurs only at a very small extent. In the contrary, the adsorption of acrylamide onto particles is very low, which is likely due to its high hydrosolubility and small size. This low affinity to soil and clay minerals could favor its transfer in surface waters and ground water, but very few studies reports AMD analysis in natural water. Moreover, several studies have demonstrated microbial degradation of acrylamide in environments amended with polyacrylamide. The biodegradation of acrylamide could thus limit its transfer in the environment. PAMs are high molecular weight polymers and are unable to pass biological membranes, so the biodegradation of these polymers requires the action of extracellular enzymes, like amidases, to degrade the carbon chain. These characteristics limit the potential of PAM biodegradation. PAM can be also subject of photodegradation and mechanical degradation. In any case, most of the studies report slow degradation rates without AMD release. The main conclusion of this review is that, despite the abundant literature dedicated to PAM use as flocculants, there is an obvious lack of pertinent and detailed data about the behavior, the fate and the impact of PAM-based flocculants in environments. Lot of work has still to be carried out to elucidate the mechanisms of degradation processes as well as to quantify the transfer of PAM and AMD in hydrosystems.

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746

747 **References**

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749 Abdel-Alim AH, Hamielec AE (1973) Shear degradation of water-soluble polymers. I. Degradation of
750 polyacrylamide in a high-shear couette viscometer. J. Appl. Polym. Sci. 17:3769–3778

751 Aly SM, Letey J (1988) Polymer and water-quality effects on flocculation of montmorillonite. Soil
752 Science Society of America Journal 52:1453-1458

753 Andersen, F.A. 2005. Amended final report on the safety assessment of polyacrylamide and
754 acrylamide residues in cosmetics, International Journal of Toxicology, 24:21-50.

755 Arrowood TJ (2008) Determining the Fate and Transport of the Acrylamide Monomer (AMD) in Soil
756 and Groundwater Systems, University of Nevada, University of Nevada at Las Vegas, Las
757 Vegas, NV, United States (USA), 132 pp

758 Avadiar L, Leong Y, Fourie A, Nugraha T (2013) Behaviours of Kaolin Suspensions with Different
759 Polyacrylamide (PAM) Flocculants under Shear. Chemeca 2013, Barton, ACT, 2013

760 Bao M, Chen Q, Li Y, Jiang G (2010) Biodegradation of partially hydrolyzed polyacrylamide by
761 bacteria isolated from production water after polymer flooding in an oil field. J. Hazard. Mater.
762 184:105-110

763 Barvenik FW (1994) Polyacrylamide characteristics related to soil applications. Soil Science 158:235-
764 243

765 Benhur M, Faris J, Malik M, Letey J (1989) Polymers as soil conditioners under consecutive irrigations
766 and rainfall. Soil Science Society of America Journal 53: 1173-1177

767 Benhur M, Letey J (1989) Effect of polysaccharides, clay dispersion, and impact energy on water
768 infiltration. Soil Science Society of America Journal 53:233-238

769 Benhur M, Malik M, Letey J, Mingelgrin U (1992) Adsorption of polymers on clays as affected by clay
770 charge and structure, polymer properties, and water-quality. Soil Science 153:349-356

771 Bicerano J (1994) Predicting key polymer properties to reduce erosion in irrigated soil. Soil Science
772 158 :255-266

773 Bottero, Lartiges (1992) Séparation liquide/solide par coagulation-floculation : les
774 coagulants/floculants, mécanismes d'agrégation, structures et densité des flocs. Mines et
775 Carrières 4

776 Bouranis DL, Theodoropoulos AG, Drossopoulos JB (1995) Designing synthetic-polymers as soil
777 conditioners. Communications in Soil Science and Plant Analysis 26 :1455-1480
778 Bouranis DL (1998) Designing synthetic soil conditioners via postpolymerization reactions. Handbook
779 of Soil Conditioners, 333-362
780 Brown L, Rhead M (1979) Liquid-chromatographic determination of acrylamide monomer in natural
781 and polluted aqueous environments. Analyst 104:391-399
782 Brown L, Bancroft KCC, Rhead MM (1980) Laboratory studies on the adsorption of acrylamide
783 monomer by sludge, sediments, clays, peat and synthetic resins. Water Research 14:779-781
784 Buranasilp K, Charoenpanich J (2011) Biodegradation of acrylamide by Enterobacter aerogenes
785 isolated from wastewater in Thailand. J Environ Sci (China) 23:396-403
786 Callebaut F, Gabriels D, De Boodt M (1979) The effect of polymer structure on soil physico-chemical
787 properties and soil water evaporation. Journal of Chemical Technology and Biotechnology.
788 29(12):723–729
789 Caulfield MJ, Qiao GG, Solomon DH (2002) Some aspects of the properties and degradation of
790 polyacrylamides. Chem Rev 102:3067-84
791 Caulfield MJ, Hao X, Qiao GG, Solomon DH (2003) Degradation on polyacrylamides. Part I. Linear
792 polyacrylamide. Polymer 44:1331-1337
793 Cavins JF, Friedman M (1968) Specific modification of protein sulfhydryl groups with alpha,beta-
794 unsaturated compounds. J Biol Chem 243:3357-60
795 Cha M, Chambliss GH (2011) Characterization of Acrylamidase isolated from a newly isolated
796 acrylamide-utilizing bacterium, Ralstonia eutropha AUM-01. Curr. Microbiol. 62:671-678
797 Cha M, Chambliss GH (2013) Cloning and sequence analysis of the heat-stable acrylamidase from a
798 newly isolated thermophilic bacterium, Geobacillus thermoglucosidasius AUT-01.
799 Biodegradation 24:57-67
800 Chamberlain P, Cole R (1996) Influence of structure and formulation on the efficacy of
801 polyacrylamides as soil stabilizers, Managing Irrigation-Induced Erosion and Infiltration with
802 Polyacrylamide, College of Southern Idaho, Twin Falls, ID, USA, pp. 83-87
803 Chang SH, Ryan ME, Gupta RK. Swiatkiewicz B (1991) The adsorption of water soluble polymers on
804 mica, talc limestone, and various clay minerals. Colloids and Surfaces 59 :59-70

Charoenpanich, J and Tani, A. (2014). Proteome Analysis of Acrylamide-induced Proteins in a Novel Acrylamide-degrader Enterobacter aerogenes by 2D Electrophoresis and MALDI-TOF-MS. CMU. J. Nat. Sci. 13:11.

Chiappa L, Mennella A, Lockhart TP, Burrafato G (1999) Polymer adsorption at the brine/rock interface: the role of electrostatic interactions and wettability. Journal of Petroleum Science and Engineering 24:113-122

Clarke PH, Drew RE, Turberville C, Brammar WJ, Ambler RP, Auffret AD (1981) Alignment of cloned amiE gene of Pseudomonas aeruginosa with the N-terminal sequence of amidase. Biosci Rep 1:299-307

Cousens DJ, Clarke PH, Drew R (1987) The amidase regulatory gene (amiR) of Pseudomonas aeruginosa. J Gen Microbiol 133:2041-52

Croll BT, Arkell GM, Hodge RPJ (1974) Residues of acrylamide in water. Water Research 8, 989-993

Crosby DG (1976): Herbicide photochemical decomposition. In: Kearney PCaK, D.D. (Editor), Berbicides : Chemistry Degradation and Mode of Action. Marcel Dekker Inc., New York, pp. 836-841

de Rosemond SJC, Liber K (2004) Wastewater treatment polymers identified as the toxic component of a diamond mine effluent. Environ. Toxicol. Chem. 23:2234– 2242.

Decker C (1989) Effect of UV radiation polymers. In: Cheremisinoff NP (Editor), Handbook of Polymer Science and Technology. Marcel Dekker Inc., New York, pp. 541-608

Deng YJ, Dixon JB, White GN, Loeppert RH, Juo ASR (2006) Bonding between polyacrylamide and smectite. Colloids and Surfaces a-Physicochemical and Engineering Aspects 281:82-91

Egorova K, Trauthwein H, Verseck S, Antranikian G (2004) Purification and properties of an enantioselective and thermoactive amidase from the thermophilic actinomycete Pseudonocardia thermophila. Appl. Microbiol. Biotechnol. 65:38-45

El-Mamouni R, Frigon JC, Hawari J, Marroni D, Guiot S (2002) Combining photolysis and bioprocesses for mineralization of high molecular weight polyacrylamides. Biodegradation 13:221-227

ElHardy OA, Abd ElHardy BM (1989) The interaction between polyacrylamide as a conditioner for sandy soils and some plant nutrients. I. Effect on the mechanical strenghy and stability and soil structure. Egyptian Journal of Soil Science 219:51-56

835 Entry JA, Sojka RE, Watwood M, Ross C (2002) Polyacrylamide preparations for protection of water
836 quality threatened by agricultural runoff contaminants. Environ Pollut 120:191-200
837 Entry JA, Sojka RE, Hicks BJ (2008) Carbon and nitrogen stable isotope ratios can estimate anionic
838 polyacrylamide degradation in soil. Geoderma 145:8-16
839 EPA US (2010) Toxicological Review of Acrylamide in Support of Summary Information on the
840 Integrated Risk Information Systems (IRIS), U.S. Environmental Protection Agency
841 European Parliament (1999) Directive 1999/45/EC concerning the approximation of the laws,
842 regulations and administrative provisions of the Member States relating to the classification,
843 packaging and labelling of dangerous preparations. Official Journal of the European Union
844 L200/1. European Union, Brussels
845 European Parliament (2006) Regulation 1907/2006/EC concerning the Registration, Evaluation,
846 Authorisation and Restriction of Chemicals (REACH). Official Journal of the European Union
847 L396/1. European Union, Brussels
848 European Union (2002). Risk assessment report on acrylamide. CAS N°: 79-06-1 (http://europa.eu.int)
849 Fitzpatrick CSB, Fradin E, Gregory J (2004) Temperature effects on flocculation, using different
850 coagulants. Water Science and Technology 50:171-175
851 Giroto JA; Teixeira AC, Nascimento CA *et al*. (2008) Photo-Fenton removal of water-soluble polymers.
852 Chemical Engineering and Processing. 47 2361-2369
853 Goodrich MS, Dulak LH, Friedman MA, Lech JJ (1991) Acute and long-term toxicity of water-soluble
854 cationic polymers to rainbow-trout (oncorhynchus-mykiss) and the modification of toxicity by
855 humic-acid. Environmental Toxicology and Chemistry 10:509-515
856 Graveling GJ, Ragnarsdottir KV, Allen GC, Eastman J, Brady PV, Balsley SD, Skuse DR (1997)
857 Controls on polyacrylamide adsorption to quartz, kaolinite, and feldspar. Geochimica Et
858 Cosmochimica Acta 61:3515-3523
859 Greenlan DJ (1963) Adsorption of polyvinyl alcohols by montmorillonite. Journal of colloid science
860 18:647-664
861 Guezennec AG, Michel C, Desroche N, Togola A, Touzé S (Submitted 2014) Microbial aerobic and
862 anaerobic degradation of acrylamide in sludges and industrial and natural waters - sand and
863 gravel quarry case study. Environmental Science and Pollution Research (SI AQUAPOL)

Hamilton M, Reinert K, Freeman MB (1994) Aquatic risk assessment of polymers. Environmental Science and Technology 28:187A-192A

Hanson AT, Cleasby JL (1990) The effect of temperature on turbulent flocculation – fluid-dynamics and chemistry. Journal American Water Works Association 82:56-73

Harford AJ, Hogan AC, Jones DR, van Dam RA (2011) Ecotoxicological assessment of a polyelectrolyte flocculant. Water Research 45: 6393-6402

Haschke H, Miles MJ, Sheppard S (2002) Adsorption of individual polyacrylamide molecules studied by atomic force microscopy. Single Molecules 3:171-172

Haveroen ME, MacKinnon MD, Fedorak PM (2005) Polyacrylamide added as a nitrogen source stimulates methanogenesis in consortia from various wastewaters. Water Res 39:3333-41

Heath AR, Bahri PA, Fawell PD, Farrow JB (2006) Polymer flocculation of calcite: Experimental results from turbulent pipe flow. AIChE Journal 52:1284-1293

Hollander AF, Somasundaran P, Gryte CC (1981) Adsorption characteristics of polyacrylamide co-polymers on sodium kaolinite. Journal of Applied Polymer Science 26:2123-2138

Holliman PJ, Clark JA, Williamson JC, Jones DL (2005) Model and field studies of the degradation of cross-linked polyacrylamide gels used during the revegetation of slate waste. Science of the Total Environment 336:13-24

Inyang HI, Bae S (2005) Polyacrylamide sorption opportunity on interlayer and external pore surfaces of contaminant barrier clays. Chemosphere 58:19-31

Jin RR, Hu WB, Hou XJ (1987) Mechanism of selective flocculation of hematite from quartz with hydrolyzed polyacrylamide. Colloids and Surfaces 26:317-331

Junqua G, Spinelli S, Gonzalez C, (2013) Occurrence and fate of acrylamide in water-recycling systems and sludge in aggregate industries Environmental Science and Pollution Research *in press* doi:10.1007/s11356-014-3022-5

Kay-Shoemake JL, Watwood ME, Lentz RD, Sojka RE (1998a) Polyacrylamide as an organic nitrogen source for soil microorganisms with potential effects on inorganic soil nitrogen in agricultural soil. Soil Biology and Biochemistry 30:1045-1052

Kay-Shoemake JL, Watwood ME, Sojka RE, Lentz RD (1998b) Polyacrylamide as a substrate for microbial amidase in culture and soil. Soil Biology and Biochemistry 30:1647-1654

Kurenkov VF, Hartan HG, Lobanov FI (2002) Degradation of polyacrylamide and its derivatives in aqueous solutions. Russian Journal of Applied Chemistry. 75:1039-1050

Labahn SK, Fisher JC, Robleto EA, Young MH, Moser DP (2010) Microbially Mediated Aerobic and Anaerobic Degradation of Acrylamide in a Western United States Irrigation Canal. Journal of Environmental Quality 39:1563-1569

Laird DA (1997) Bonding between polyacrylamide and clay mineral surfaces. Soil Science 162:826-832

LaMer VK, Healvy TW (1963) Adsorption-flocculation reactions of macromolecules at the solid-liquid interface. Review of Pure and Applied Chemistry 13:112-132

Lande SS, Bosch SJ, Howard PH (1979) Degradation and leaching of acrylamide in soil. J. Environ. Qual. 8:133-137

Lavrov KV, Zalunin IA, Kotlova EK, Yanenko AS (2010) A new acylamidase from Rhodococcus erythropolis TA37 can hydrolyze N-substituted amides. Biochemistry (Mosc) 75:1006-1013

Lecourtier J, Lee LT, Chauveteau G (1990) Adsorption of polyacrylamide on siliceous minerals. Colloids and Surfaces 47:219-231

Lee JJ, Fuller GG (1985) Adsorption and desorption of flexible polymer-chains in flowing systems. Journal of Colloid and Interface Science 103:569-577

Lee LT, Somasundaran P (1991) Effect of inorganic and organic additives on the adsorption of nonioninc polyacrylamide on hematite. Journal of Colloid and Interface Science 142:470-479

Lentz RD, Sojka RE (2000) Applying polymers to irrigation water: Evaluating strategies for furrow erosion control. Transactions of the Asae 43:1561-1568

Lentz RD, Sojka RE, Mackey BE (2002) Fate and efficacy of polyacrylamide applied in furrow irrigation: Full-advance and continuous treatments. Journal of Environmental Quality 31:661-670

Leong YK, Creasy DE, Boger DV, Nguyen QD (1987) Rheology of brown coal-water suspensions. Rheologica Acta 26:291-300

Liber K, Weber L, Levesque C (2005) Sublethal toxicity of two wastewater treatment polymers to lake trout fry (*Salvelinus namaycush*). Chemosphere 61:1123-1133

Liu L, Wang Z, Lin K, Cai W (2012) Microbial degradation of polyacrylamide by aerobic granules. Environ Technol 33:1049-54

923 Liu ZH, Cao YM, Zhou QW, Guo K, Ge F, Hou JY, Hu SY, Yuan S, Dai YJ (2013) Acrylamide
924 biodegradation ability and plant growth-promoting properties of Variovorax boronicumulans
925 CGMCC 4969. Biodegradation In Press
926 Lu JH, Wu L, Letey J (2002) Effects of soil and water properties on anionic polyacrylamide sorption.
927 Soil Science Society of America Journal 66:578-584
928 Lu JH, Wu LS (2013) Polyacrylamide distribution in columns of organic Matter-Removed Soils
929 following Surface Application. J. Environ. Qual. 32:674-680
930 Lurie M, Rebhun M (1997) Effect of properties of polyelectrolytes on their interaction with particulates
931 and soluble organics. Water Science and Technology 36:93-101
932 Lyklema J, Fleer GJ (1987) Electrical contributions to the effect of macromolecules on colloid stability.
933 Colloids and Surfaces 25:357-368
934 Ma Y, Yu H, Pan W, Liu C, Zhang S, Shen Z (2010) Identification of nitrile hydratase-producing
935 Rhodococcus ruber TH and characterization of an amiE-negative mutant. Bioresour. Technol.
936 101:285-291
937 McCollister DD, Oven F & Rowe VK (1964) Toxicology of acrylamide. Toxicol. Appl. Pharmacol.
938 6:172–181
939 Makhongela HS, Glowacka AE, Agarkar VB, Sewell BT, Weber B, Cameron RA, Cowan DA, Burton
940 SG (2007) A novel thermostable nitrilase superfamily amidase from Geobacillus pallidus
941 showing acyl transfer activity. Appl. Microbiol. Biotechnol. 75:801-811
942 Malik M, Letey J (1991) Adsorption of polyacrylamide and polysaccharide polymers on soil materials.
943 Soil Science Society of America Journal 55:380-383
944 Malik M, Nadler A, Letey J (1991) Mobility of polyacrylamide and polysaccharide polymer through soil
945 materials. Soil technology 4:255-263
946 Matsuoka H, Ishimura F, Takeda T, Hikuma M (2002) Isolation of polyacrylamide-degrading
947 microorganisms from soil. Biotechnology and Bioprocess Engineering 7:327-330
948 Michaels AS, Morelos O (1955) Polyelectrolyte adsorption by kaolinite. Industrial and Engineering
949 Chemistry 47, 1081-1809
950 Molak, V. Acrylamide: A Review of the Literature in NIOH and NIOSH Basis for an Occupational
951 Health Standard. US Department of Health and Human Services, 1991.
952 Mortland (1970) Clay-organic complexes and interactions. Advances in Agronomy 22:75-117

953 Mpofu P, Addai-Mensah J, Ralston J (2004) Temperature influence of nonionic polyethylene oxide and
954 anionic polyacrylamide on flocculation and dewatering behavior of kaolinite dispersions.
955 Journal of Colloid and Interface Science 27: 145-156
956 Nabzar L, Pefferkorn E, Varoqui R (1984) Polyacrylamide sodium kaolinite interactions – flocculation
957 behavior of polymer clay suspensions. Journal of Colloid and Interface Science 102:380-388
958 Nabzar L, Pefferkorn E, Varoqui R (1988) Stability of polymer clay suspensions – the polyacrylamide
959 sodium kaolinite system. Colloids and Surfaces 30:345-353
960 Nadler A, Letey J (1989) Adsorption-isotherms of polynions on soils using tritium labeled compounds.
961 Soil Science Society of America Journal 53:1375-1378
962 Nadler A, Malik M, Letey J (1992) Desorption of polyacrylamide and polysaccharide polymers from
963 soil materials. Soil Technology 5:91-95
964 Nagashiro W, Tsunoda T, Tanaka M, Oikawa M (1975) Degradation of polyacrylamide molecules in
965 aqueous-solutions by high-speed strirring. Bulletin of the Chemical Society of Japan 48:2597-
966 2598
967 Nakamiya K, Kinoshita S (1995) Isolation of polyacrylamide-degrading bacteria. Journal of
968 Fermentation and Bioengineering 80:418-420
969 Nawaz MS, Franklin W, Cerniglia CE (1993) Degradation of acrylamide by immobilized cells of a
970 Pseudomonas sp. and Xanthomonas maltophilia. Can. J. Microbiol. 39:207-212
971 Nawaz MS, Khan AA, Seng JE, Leakey JE, Siitonen PH, Cerniglia CE (1994) Purification and
972 characterization of an amidase from an acrylamide-degrading Rhodococcus sp. Appl Environ
973 Microbiol 60:3343-8
974 Nawaz MS, Khan AA, Bhattacharayya D, Siitonen PH, Cerniglia CE (1996) Physical, biochemical, and
975 immunological characterization of a thermostable amidase from Klebsiella pneumoniae NCTR
976 1. J. Bacteriol. 178:2397-2401
977 Nawaz MS, Billedeau SM, Cerniglia CE (199): Influence of selected physical parameters on the
978 biodegradation of acrylamide by immobilized cells of Rhodococcus sp. Biodegradation 9:381-
979 387
980 Nguyen QD, Boger DV (1985) Thixotropic behaviour of concentrated bauxite residue suspensions
981 Rheol Acta 24:427-437

982 Nguyen QD, Boger DV (1998) Application of rheology to solving tailings disposal problems.
983 International Journal of Mineral Processing 54:217-233
984 Ohtaki A, Murata K, Sato Y, Noguchi K, Miyatake H, Dohmae N, Yamada K, Yohda M, Odaka M
985 (2010) Structure and characterization of amidase from Rhodococcus sp. N-771: Insight into
986 the molecular mechanism of substrate recognition. Biochim. Biophys. Acta 1804:184-192
987 Parfitt RL, Greenland JD (1970) Adsorption of polysaccharides by montmorillonite. Soil Science
988 Socienty of America Journal 34:562-866
989 Paterson RW, Abernathy FH (1970) Turbulent flow drag reduction and degradation with dilute polymer
990 solutions. J. Fluid. Mech 43:689-710
991 Pefferkorn E, Nabzar L, Varoqui R (1987) Polyacrylamide Na-kaolinite interactions – effect of
992 electrolyte concentration on polymer adsorption. Colloid and Polymer Science 265:889-896
993 Pereira AS, Soares EJ (2012) Polymer degradation of dilute solutions in turbulent drag reducing flows
994 in a cylindrical double gap rheometer device. J. Non Newtonian Fluid Mech. 179-180:9-22
995 Potts JR, Clarke PH (1976) The effect of nitrogen limitation on catabolite repression of amidase,
996 histidase and urocanase in Pseudomonas aeruginosa. J Gen Microbiol 93:377-87
997 Povkh LI, Chernyuk VV (1986) An experimental investigation of the effect of a polyacrylamide additive
998 on the pressure drop in an expansion Journal of engineering physics 51:1001-1004
999 Pradip YAA, Fuerstenau DW (1980) The adsorption of polyacrylamide flocculants on apaties. Colloid
1000 and Polymer Science 258:1343-1353
1001 Rabek JF (1996) In Photodegradation of Polymers: Physical Characteristics and Applications.
1002 Springer-Verlag. Berlin
1003 Rasteiro MG, Garcia FAP, Ferreira P, Blanco A, Negro C, Antunes E (2008) Evaluation of flocs
1004 resistance and reflocculation capacity using the LDS technique. Powder Technology 183:231-
1005 238
1006 Ren G-m, Sun D-z, Chung Jong S (2006) Kinetics study on photochemical oxidation of polyacrylamide
1007 by ozone combined with hydrogen peroxide and ultraviolet radiation. Journal of Environmental
1008 Sciences-China 18:660-664
1009 Rho T, Park J, Kim C, Yoon HK, Suh HS (1996) Degradation of polyacrylamide in dilute solution.
1010 Polymer Degradation and Stability 51:287-293

1011 Ruehrwein RA, Ward DW (1952) Mechanism of clay aggregation by polyelectrolytes. Soil Science
1012 73:485-492
1013 Santoshkumar M, Nayak AS, Anjaneya O, Karegoudar TB (2010) A plate method for screening of
1014 bacteria capable of degrading aliphatic nitriles. J. Ind. Microbiol. Biotechnol. 37:111-115
1015 Sathesh Prabu C, Thatheyus AJ (2007) Biodegradation of acrylamide employing free and immobilized
1016 cells of Pseudomonas aeruginosa. International Biodeterioration & Biodegradation 60:69-73
1017 Sato T, Ruch R (1980) Stabilization of colloidal dispersions by polymer adsorption. In: Dekker (Editor),
1018 Surfactant science serie. Marcel Dekker Inc., New York
1019 Scott JP, Fawell PD, Ralph DE, Farrow JB (1996) The shear degradation of high-molecular-weight
1020 flocculant solutions. Journal of Applied Polymer Science 62:2097-2016
1021 Senden TJ, Di Meglio JM, Silberzan I (2000) The conformation of adsorbed polyacrylamide and
1022 derived polymers. Comptes Rendus De L Academie Des Sciences Serie Iv Physique
1023 Astrophysique 1 :1143-1152
1024 Seybold CA (1994) Polyacrylamide review: Soil conditioning and environmental fate. Communications
1025 in Soil Science and Plant Analysis 25:2171-2185
1026 Shanker R, Ramakrishna C, Seth PK (1990) Microbial degradation of acrylamide monomer. Arch.
1027 Microbiol. 154:192-198
1028 Sharma M, Sharma N, Bhalla T (2009) Amidases: versatile enzymes in nature. Reviews in
1029 Environmental Science and Biotechnology 8:343-366
1030 Shukor MY; Gusmanizar N; Azmi NA et al. (2009a) Isolation and characterization of an acrylamide-
1031 degrading Bacillus cereus. Journal of environmental biology. 30(1)57-64
1032 Shukor MY, Gusmanizar N, Ramli J, Shamaan NA, MacCormack WP, Syed MA (2009b) Isolation and
1033 characterization of an acrylamide-degrading Antarctic bacterium. J. Environ. Biol. 30:107-112
1034 Smith, EA and Oehme FW (1993) Rapid direct analysis of acrylamide residue in polyacrylamide
1035 thickening agents by HPLC. Journal of Chromatographic Science 31:192-195.
1036 Smith EA, Prues SL, Oehme FW (1996) Environmental degradation of polyacrylamides .1. Effects of
1037 artificial environmental conditions: Temperature, light, and pH. Ecotoxicology and
1038 Environmental Safety 35:121-135
1039 Smith EA, Prues SL, Oehme FW (1997) Environmental degradation of polyacrylamides .2. Effects of
1040 environmental (outdoor) exposure. Ecotoxicology and Environmental Safety 37:76-91

1041 Sojka RE, Entry JA (2000) Influence of polyacrylamide application to soil on movement of
1042 microorganisms in runoff water. Environ Pollut 108:405-12
1043 Sojka RE, Bjorneberg DL, Entry JA, Lentz RD, Orts WJ (2007) Polyacrylamide in Agriculture and
1044 Environmental Land Management. Advances in Agronomy 92:75-162
1045 Spicer PT, Pratsinis SE, Raper J, Amal R, Bushell G, Meesters G (1998) Effect of shear schedule on
1046 particle size, density, and structure during flocculation in stirred tanks. Powder Technology
1047 97:26-34
1048 Spofford TL, Pfeiffer KL (1996) Agricultural irrigation polyacrylamide application standard, Managing
1049 Irrigation-Induced Erosion and Inflitration with Polyacrylamide, College of Southern Idaho,
1050 Twin Falls, Id USA
1051 Stephens SH (1991) Final report on the safety of polyacrylamide. Journal of the American college of
1052 toxicology 10:193-202
1053 Stutzmann T, Siffert B (1977) Contribution to adsorption mechanism of acetamide and polyacrylamide
1054 on to clays. Clays and Clay Minerals 25:392-406
1055 Suzuki K, Sugiyama A, Nakazato K (1978) Study of acrylamide-gel chromatography 3 spherical gels of
1056 polyacrylamide imdized by heat-treatment. Nippon Kagaku Kaishi, 1385-1389
1057 Suzuki K, Nakazato K, Takasaki T (1979) Study of acrylamide-gel chromatography 4 spherical gels of
1058 polyacrylamide co-polymerized with acrylonitrile. Nippon Kagaku Kaishi, 1327-1331
1059 Syed MA, Ahmad SA, Kusnin N, Shukor MY (2012) Purification and characterization of amidase from
1060 acrylamide-degrading bacterium Burkholderia sp. strain DR.Y27. African Journal of
1061 Biotechnology 11:329-336
1062 Tanaka H, Odberg L, Wagberg L, Lindstrom T (1990) Adsorption of cationic polyacrylamide onto
1063 monodisperses polystyrene lattices and cellulose fiber – effect of molecular-weight and
1064 charge-density of cationic polyacrylamides. Journal of Colloid and Interface Science 13: 219-
1065 228
1066 Tang S, Ma Y, Shiu C (2001) Modeling the mechanical strength of fractal aggregates. Colloids Surf.
1067 Physicochem. Eng. Aspects 180:7-16
1068 Taylor ML, Morris GE, Self PG, Smart RS (2002) Kinetics of adsorption of high molecular weight
1069 anionic polyacrylamide onto kaolinite: The flocculation process. Journal of Colloid and
1070 Interface Science 250: 28-36

1071 Tekin N, Demirbas O, Alkan M (2005) Adsorption of cationic polyacrylamide onto kaolinite.
1072 Microporous and Mesoporous Materials 85:340-350
1073 Tekin N, Dincer A, Demirbas O, Alkan M (2006) Adsorption of cationic polyacrylamide onto sepiolite.
1074 Journal of Hazardous Materials 134:211-219
1075 Tekin N, Dincer A, Demirbas O, Alkan M (2010) Adsorption of cationic polyacrylamide (C-PAM) on
1076 expanded perlite. Applied Clay Science 50:125-129
1077 Thanyacharoen U, Tani A, Charoenpanich J (2012) Isolation and characterization of Kluyvera
1078 georgiana strain with the potential for acrylamide biodegradation. J Environ Sci Health A Tox
1079 Hazard Subst Environ Eng 47:1491-9
1080 Theng BKG (1979) Formation and properties of clay-polymer complexes. Developement in Soil
1081 Sciences 9:9-11
1082 Theng BKG (1982) Clay-polymer interactions - summary and perspectives. Clays and Clay Minerals
1083 30:1-10
1084 Togola A, Coureau C, Guezennec AG, Touzé S (Submitted 2014). A sensitive analytical procedure for
1085 acrylamide in environmental water samples by offline SPE-UPLC/MS/MS. Environ Sci Pollut
1086 Res (SI AQUAPOL)
1087 Touzé S, Guerin V, Guezennec AG, Binet S, Togola A (2014). Dissemination of acrylamide monomer
1088 from polyacrylamide based flocculant use - sand and gravel quarry case study. Environ Sci
1089 Pollut Res (SI AQUAPOL)
1090 UNPG (2013) Polyacrylamide based flocculant used in quarries (in French). Union National des
1091 Producteurs de Granulats UNPG
1092 Van de Ven TGM (1994) Kinetic aspects of polymer and polelectrolyte adsorption on surfaces.
1093 Advances in Colloid and Interface Science 48:121-140
1094 Ver Vers LM (1999) Determination of acrylamide monomer in polyacrylamide degradation studies by
1095 high-performance liquid chromatography. Journal of Chromatographic Science 37:486-494
1096 Vlachogiannis M, Liberatore MW, McHugh AJ, Hanratty TJ (2003) Effectiveness of a drag reducing
1097 polymer: Relation to molecular weight distribution and structuring. Physics of Fluids 15:3786-
1098 3794
1099 Wade JHT, Kumar P (1972) Electronic microscope studies of polymer degradation. J. Hydronaut. 6-40

1100 Wakaizumi M, Yamamoto H, Fujimoto N, Ozeki K (2009) Acrylamide degradation by filamentous fungi
1101 used in food and beverage industries. J. Biosci. Bioeng. 108:391-3
1102 Wampler DA, Ensign SA (2005) Photoheterotrophic metabolism of acrylamide by a newly isolated
1103 strain of Rhodopseudomonas palustris. Appl. Environ. Microbiol. 7: 5850-5857
1104 Weideborg M, Kallqvist T, Odegard KE, Sverdrup LE, Vik EA (2001) Environmental risk assessment of
1105 acrylamide and methylolacrylamide from a grouting agent used in the tunnel construction of
1106 Romeriksporten, Norway. Water Research 35:2645-2652
1107 Wen Q, Chen Z, Zhao Y, Zhang H, Feng Y (2010) Biodegradation of polyacrylamide by bacteria
1108 isolated from activated sludge and oil-contaminated soil. J. Hazard. Mater. 175:955-959
1109 Wilson S, Drew R (1991) Cloning and DNA sequence of amiC, a new gene regulating expression of
1110 the Pseudomonas aeruginosa aliphatic amidase, and purification of the amiC product. J
1111 Bacteriol 173:4914-21
1112 Wilson SA, Wachira SJ, Drew RE, Jones D, Pearl LH (1993) Antitermination of amidase expression in
1113 Pseudomonas aeruginosa is controlled by a novel cytoplasmic amide-binding protein. Embo J
1114 12:3637-42
1115 Wilson SA, Drew RE (1995) Transcriptional analysis of the amidase operon from Pseudomonas
1116 aeruginosa. J Bacteriol 177:3052-7
1117 World Health Organization (1985) Environmental Health Criteria 1985, 49, 1. International programme
1118 on chemical safety Web. http://www.inchem.org/documents/ehc/ehc/ehc49.htm
1119 Woodrow JE, Seiber JN, Miller GC (2008) Acrylamide release resulting from sunlight irradiation of
1120 aqueous polyacrylamide/iron mixtures. Journal of Agricultural and Food Chemistry 56:2773-
1121 2779
1122 Yamada H, Asano Y, Hino T, Tani Y (1979) Microbial utilization of acrylonitrile. Journal of fermentation
1123 technology 5: 8-14
1124 Yeung A, Gibbs A, Pelton R (1997) Effect of shear on the strength of polymer-induced flocs. Journal of
1125 Colloid and Interface Science 196:113-115
1126 Yeung AKC, Pelton R (1996) Micromechanics: A new approach to studying the strength and breakup
1127 of flocs. Journal of Colloid and Interface Science 184:579-585

Young MH, Tappen JJ, Miller GC, Carroll S., Susfalk R.B. (2007). Risk Characterization: Using Linear Anionic Polyacrylamide to Reduce Water Seepage from Unlined Water Delivery Canal Systems. Publication no. 41226. Desert Research Institute, Las Vegas, NV.

$$n\ \underset{\underset{O}{\|}}{CH_2=CH-C-NH_2}\ +m\ \underset{\underset{O}{\|}}{CH_2=CH-C-OH}\ +NaOH\rightarrow\left[\begin{array}{c}CH_2-CH\\ |\\ C=O\\ |\\ NH_2\end{array}\right]_n-\left[\begin{array}{c}CH_2-CH\\ |\\ C=O\\ |\\ ONa\end{array}\right]_m$$

Fig. 1 Synthesis pathway of anionic PAMs

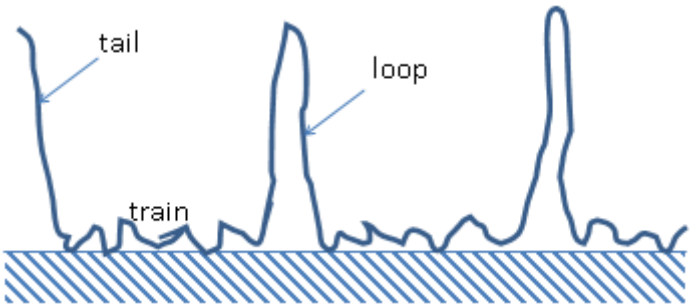

Fig. 2 Conformation of a polymer adsorbed onto the surface of a mineral particle

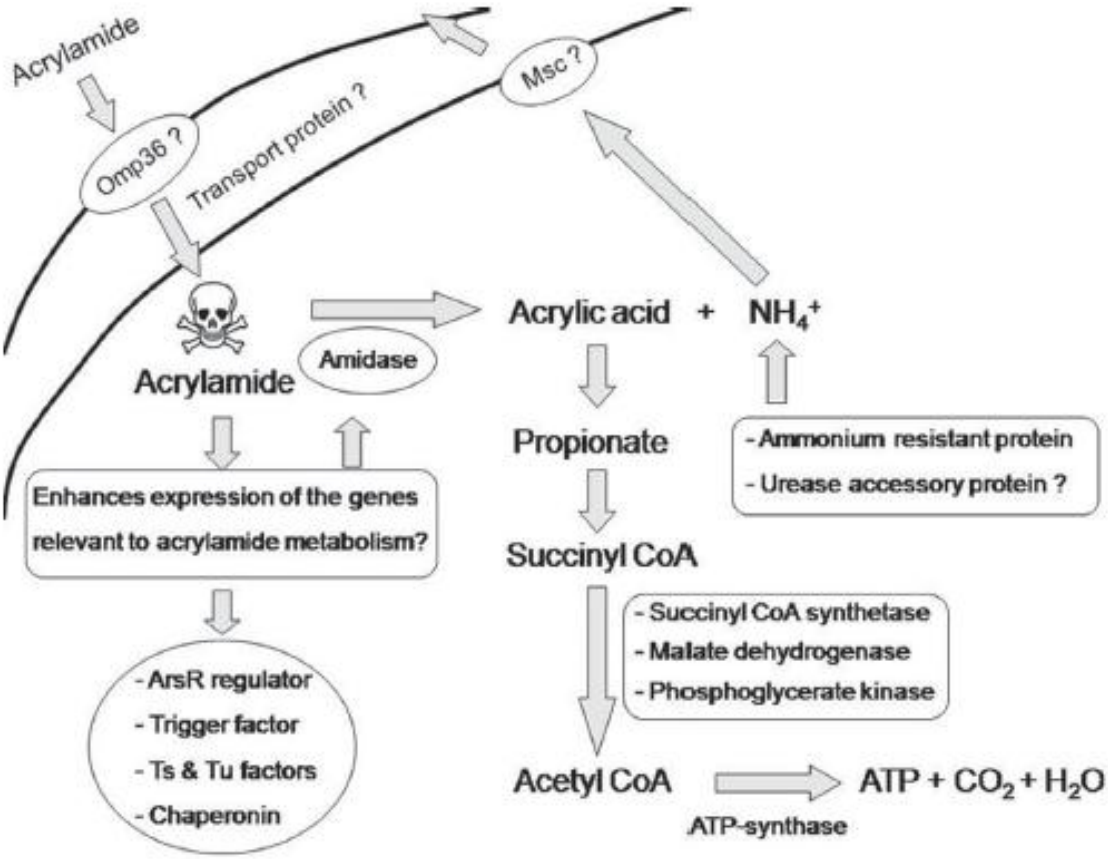

Fig. 3 Metabolic pathway of AMD degradation in Enterobacter aerogenes proposed by Charoenpanich and Tani (2014).

Table 1 Aerobic biodegradation of acrylamide in various environmental samples

References	Acrylamide concentration	Temperature	Lag time	Time for complete AMD degradation
Labahn *et al*. (2010)	50 µg.L^{-1}	15°C	No degradation observed after 72 h	
		25°C	0-12h	24 h
Croll (1973)	10 µg.L^{-1}	Non indicated	5h-50h	50h-300h
Brown (1979)	5 mg.L^{-1}	20°C	75h	125 h
Vers (1999)	1,5-2,5 mg.L^{-1}	Non indicated	0h	from 480 h to more than 1100 h

Table 2 Molecular weight, pH and temperature optima of amidases purified from AMD-degrading bacteria.

Bacterial strains	Molecular weight (kDa)	Optimum pH	Optimum temperature	Reference
Geobacillus thermoglucosidasius AUT-01	38.0	6.2	70°C	Cha and Chambliss, 2013
Geobacillus pallidus BTP-5x MTCC 9225	38.5	8.0	60°C	Sharma *et al.* 2012
Ralstonia eutropha AUM-01	38.0	6.3	55°C	Cha and Chambiss, 2011
Variovorax boronicumulans CGMCC 4969	42.0	ND*	ND*	Liu *et al.* 2013
Burkholderia sp. DR.Y27	47.0	8.0	40°C	Syed *et al.* 2012
Rhodococcus sp.	44.5	8.5	40°C	Nawaz *et al.* 1994
Rhodococcus sp. N-771	54.7	5.9	55°C	Ohtaki *et al.* 2010
Klebsiella pneumoniae NCTR 1	62.0	7.0	65°C	Nawaz *et al.* 1996
Geobacillus pallidus RAPc8	38.0	7.0	50°C	Makhongela *et al.* 2007
Pseudonocardia thermophila DSMZ 43832	52.0	7.0	70°C	Egorova *et al.* 2004
Rhodococcus erythropolis TA37	55.0	8.0	55°C	Lavrov *et al.* 2010

* ND: Not Determined